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Property Modification of a De-icing Agent

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Property Modification of a De-icing Agent

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Abstract:	This report provides an overview of a study which investigated the feasibility of using polymers to reduce the high cost of de-icing open graded friction courses. Possible methods are discussed, along with a series of tests designed to determine their effectiveness. The results of the tests are summarized and interpreted. The following conclusions are presented: • Viscosity enhancement is not feasible as a means of reducing salt consumption on open graded friction courses. • Encapsulating road salt using a sprayed-on coating of hydroxyethylcellulose is both feasible and effective. The following recommendations are made: • Further study should be done to ensure that drainage through actual road surfaces is accurately modelled by the road core samples. • The spray encapsulation process should be scaled up to make tonne quantities of hydroxyethylcellulose-coated salt available. • Road testing of hydroxyethylcellulose-coated salt should be done. This testing should be used to determine the effectiveness of the treatment and to optimize its use in real conditions.
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1. INTRODUCTION

The Ministry of Transportation of Ontario recently began to utilize a new open graded friction course in certain areas. This new road surface is advantageous when compared with traditional asphalt surfaces in that it is porous. This prevents hydroplaning by allowing drainage through the road surface, and also causes a significant reduction in traffic generated noise.

This new road surface also has its drawbacks. It's price is approximately quadruple that of normal asphalt roadway. The increased drainage rates, due to the porosity of the road, cause much of the road salt applied to be drained off as a concentrated brine (still possessing much of its de-icing potential). This necessitates more frequent salt applications. This need for more frequent de-icing is costly as it requires more manpower, equipment and salt. While rock salt in itself is relatively inexpensive (around $35/tonne) its use is harmful to the environment, causing an estimated $10 damage for every $1 of salt used (cf reference to O'Toole, p.28).

It is the purpose of this study to discover a means of reducing the amount of salt used on these open graded friction courses, and to thereby lower the cost of de-icing these roads. By cutting down on the amount of salt lost through drainage, both the amount of salt, and the frequency of application would be lessened. This would be favourable both from an environmental and from an economic viewpoint.

When one considers the processes by which the salt is removed from the

surface of this new road type, it becomes apparent that one of two conditions must be met if the road life of the salt (the length of time the salt remains effective de-icing the road surface) is to be increased. The rate of drainage of the dissolved salt must be reduced or the dissolution of the solid salt must be retarded. Viscosity enhancement of the brine may serve to reduce its rate of drainage, while encapsulation of the solid salt may serve to inhibit its dissolution.

2. MATERIALS

The initial step in this study was to find materials potentially suitable for either viscosity enhancement or for encapsulation. Polymers, due to their unique properties in solution, and their great utility as coatings, are excellent candidate materials for both methods of salt retention. The polymers used to thicken the brine must be water-soluble since it is necessary for a polymer to go into solution in order for it to be effective as a viscosity enhancement agent. Water-soluble polymers are also the candidate of choice for encasing the road salt, due to the prohibitive cost of nonaqueous solvents. The use of water-soluble polymers would also prevent polymer build-up on the roadway.

A literature search was necessary so that only the most promising of the many water-soluble polymers commercially available could be focused on. The five classes selected were guar gum (GG), hydroxyethylcellulose (HEC), poly(vinyl alcohol) (PVA), poly(acrylamide) (PAA), and sodium alginate (NaAlg). These were selected using the primary criteria of availability, solubility in cold water and cost. Other considerations were viscosity in water, pH stability, environmental compatibility, gelling properties, resistance to salting out, system of grading, and origins (man-made or natural). Based on cost estimations as outlined in Appendix A, it is believed polymer usage at a level of 1% would be acceptable since the use of polymer at this level would only triple the cost of the salt.

Tests were done to acquire information about road salt obtained from the Ministry of Transportation of Ontario. The size and shape of its constituent

particles was of particular interest. This information is needed since the solid salt is an essential component in the encapsulation work.

The sample of road salt was 97% soluble in water. The insoluble portion was primarily composed of very fine, dust-like particles. The sample as a whole was composed of irregularly shaped particles which passed through a 16 mm mesh. A breakdown of the size distribution is given in Table 1. Of particular note is the fact that over 80% of the salt is retained by a 2 mm mesh. This is auspicious since these particles seem large enough for encapsulation without aggregation.

Some core samples of an open graded friction course were also obtained. Each was composed of an asphalt cylinder consisting of two layers. The top layer was made up of a porous asphalt, the porosity arising from the use of aggregate of controlled particle size. The porosity allowed both vertical and lateral flow through this layer. Under this was a normal asphalt layer which is much denser an impermeable to water. From these samples six test rigs were constructed as illustrated in Figure 9. These rigs were used in both the viscosity enhancement work and in the encapsulation work.

3. METHODS

3.1 Viscosity Enhancement

Viscosity enhancement of the brine resulting from de-icing the roadway should cause a proportional increase in the residence time of the brine on the road. This should occur since, under normal conditions, the rate of drainage of a liquid through a porous surface should be inversely proportional to its viscosity. Thus, in order to know how the residence time of a brine on the road will be affected by a polymer, it is necessary to know the degree to which the polymer enhances viscosity and to ensure that drainage through the road behaves as predicted. The enhanced brine viscosity could be achieved simply by applying a blend of the water-soluble polymer and salt to the road.

3.1.1 Solution Viscosities

For measuring their viscosity enhancing power at higher concentrations, 1% aqueous solutions of each polymer were prepared. This was done by mixing the dry polymer into water at room temperature (except for PVA which required water at 80 deg. C). These solutions were then cooled to 3 deg. C and their viscosities measured using a Brookfield LVT viscometer. All of the solutions, with the exception of the PVA solution (which was deemed unsuitable for viscosity enhancement since it required heating to get it into solution), were then diluted to 0.5% and 0.1% polymer by weight in a 2.5% NaCl solution. The viscosities were then measured by the same procedure as the 1% solutions. In order to detect non-Newtonian behaviour, viscosities were measured at several spin rates (and hence shear rates) whenever possible in

the above cases. The PAA solutions were noted to have a strong lubricating effect and were consequently deemed unsuitable for viscosity enhancement. A rough calculation (see Appendix A) estimates a lower limit on the concentration of the polymer in brine to be 0.005%. This necessitated the measurement of the viscosities of lower concentration solutions of the three remaining polymers. A Cannon-Fenske Routine Viscometer was used. The viscosities of 0.05% and 0.005% solutions of each polymer in deionized water were measured.

3.1.2 Road Drainage

The times taken for 150 mL aliquots of solutions (of known viscosity) to pass through dry road core test rigs were used to measure the effect of viscosity on the rate of drainage through open graded roadway.

The effect of the pressure head on the flow rate through these test rigs was also examined. This is discussed in Appendix B.

3.2 Encapsulation

The encapsulation of road salt in a water-soluble polymer should prolong the road life of the salt for the following reasons. Initially, contact between the salt and water would be prevented by the coating. The water would then slowly swell the coating. After the coating had become swollen water could begin to diffuse through it. The water would then start to dissolve the salt, but the dissolution would be hindered since the water and dissolved salt would

have to diffuse through the polymer. Finally, the coating would dissolve and provide viscosity enhancement to the brine. Thus, the encapsulation approach appears to have great potential to increase the effectiveness of road salt on open graded surfaces since it combined inhibited dissolution with viscosity augmentation. Accordingly, encapsulation was investigated to see if it significantly enhances the road life of the salt. It should be mentioned that coating salt using aqueous solutions is very difficult since the surface to which the polymer is supposed to adhere is dissolving. The use of nonaqueous systems is, however, ruled out due to their prohibitive solvent costs.

This part of the study progressed in two stages. The initial stage consisted of attempts to encapsulate the salt using "wet" (immersion) methods of encapsulation. The second stage (an attempt to overcome shortcomings of the earlier "wet" testing) consisted of attempts to coat the salt in polymer using a "dry" (spray) method. In both stages several methods were used to test the effect of coating the salt. Several different test methods were used due to the difficulty in finding a test which was both repeatable and an effective measure of the salt's behaviour if left undisturbed on the road.

3.2.1 Wet Methods

The term wet methods is used to describe this set of tests since in all cases the salt used in them was coated by immersion in an aqueous solution followed by the evaporating off of the water.

Manual Coating - This was the first work done in encasing the salt and

proceeded as follows. A 1% aqueous solution of each polymer was prepared. Each solution then had poured into it salt which was passed through a 12.5 mm mesh but was retained by an 8 mm mesh. This fraction of the salt was selected for its large size which made it easy to separate individual pieces. Each mixture was then poured out onto a glass plate. The individual salt pieces were then manually separated and the glass plates placed in an oven. This yielded polymer coated salt.

Some salt was also coated in calcium alginate (CaAlg), a crosslinked gel which swells but is practically insoluble in water, formed by crosslinking alginate ions with calcium ions. The encapsulation technique was similar to that used above. In an attempt to localize the gelling to the surfaces of individual salt particles the salt was immersed in a saturated calcium chloride solution and then dried on a glass sheet. The calcium treated salt was then poured into a 1% NaAlg solution and dried as above.

To test the encapsulated salt for impeded dissolution, the conductance of a fixed volume of deionized water was recorded along with time as a salt particle was allowed to dissolve in it. This was done at between 2 and 4 deg. C. Self-consistent results were obtained through the use of large pieces of salt having similar mass (to minimize surface area variations) and constant bubbling (causing constant agitation and hence preventing concentration gradients).

These results could be used to get a relative measure of the rates of dissolution of the coated salts. It was necessary to choose an arbitrary

measure of the rate of dissolution of the salt, since the shape of the conductance versus time plots (see Figure 1 for typical plots) is complex, and since the rate of dissolution does not correspond directly to the rate of change of conductance. The slope of the line connecting the point representing the introduction of salt into the system and the point representing 80% of the final conductance value was chosen to be this measure.

Drum Drying - Encapsulation was pursued further because of the encouraging results of the above work. However, if the treated salt was to represent a feasible product then it was felt a coating method paralleling an industrial one should be used. The method chosen was to place the salt in a rotating heated, baffled, container (effectively a scaled down drum dryer) along with the polymer solution. Since the water would be evaporated off, it was expected that the continual reapplication of a solution of increasing concentration to the surface of the salt would yield a more complete and adherent coating than those obtained in the initial work.

An estimation of the cost of encapsulation (see Appendix A) gives the cost of a 1% polymer by weight encapsulated salt to be roughly triple that of untreated salt. Since treatment in this price range is inexpensive (when compared with the cost of the environmental damage done by salt), it was decided to try coating the salt at a 1% polymer level.

To minimize variability in test results due to fluctuating surface area to mass ratios, it was decided to use only one fraction of the salt based on size.

The salt in the 2.4 mm - 4.8 mm range would be used for all further work since it constitutes 40% of the salt as a whole and was deemed representative.

Further work was focussed on the use of HEC and/or gel system since these gave the most encouraging results in the earlier encapsulation work.

The first gel system used was that of CaAlg. It was applied to the salt by first drying 75mL of 2% $CaCl_2$ on 200g of salt. Then 200mL of 1% NaAlg was dried on the treated salt. The resultant product contained 0.75% $CaCl_2$ and 1% NaAlg by weight.

The second gel system used was that formed by crosslinking GG with borate ions. The salt was treated by first drying 100mL of 2% borax on 200g salt. This was followed by the application of 200mL of a weakly acidified 1% GG solution. As this solution was dried onto the salt it was slowly made basic (pH 8) by the addition of a NaOH solution. This was necessary since the gel is only formed under basic conditions. The dry mixture was 1% borax and 1% GG by weight. The HEC coated salt was produced by consecutively drying 2-100mL 1% HEC solutions onto 200g salt. This yielded a product containing 1% HEC.

Salt treated by a combination of one fo the above gels and HEC was also made. The gelling agent (borax or $CaCl_2$) was dried onto 200g salt as 100mL of 2% solution. This was followed by successive drying of 2-100mL 0.5% - 0.5% HEC - crosslinkable polymer solutions. In the case of GG the solutions were made basic as they dried. The net yield was a product of composition 1%

gelling agent and 0.5% of each of the two polymers.

The products of the drum dryer coating techniques were then tested using the road core test rigs described earlier. The road cores were cooled to -2 deg. C and 25g crushed ice was placed in the tube of each. On each was spread 10g of salt. They were maintained at -2 deg. C until all the ice had melted after which any salt remaining in the test rig was recovered and weighed. This gave a measure of the amount of salt lost in melting 25g of ice and thus a means of comparing the various salt treatments.

3.2.2 Dry Methods

Flaws were observed in the coatings obtained using the wet encapsulation techniques. These flaws were judged to be a result of the surface of the wet salt dissolving as the coating was applied. Thus, a process which minimized the wetting of the salt was sought as it was believed that this would minimize the flaws in the coating.

Spray Coating - A method whereby agitated salt is sprayed with a fine mist of polymer solution while simultaneously being dried by a heated air stream was chosen after consultation with an expert in industrial process design (Dr. M.E. Fayed of Ryerson Polytechnical Institute).

Apparatus was constructed as illustrated in Figure 13.

Only HEC and CaAlg coatings were tried since these were determined to

be the most successful from the earlier work.

The polymer (HEC or NaAlg) was applied as a 1% solution in all cases. By using either 100mL or 200mL per 100g salt, a product that was 1% or 2% respectively polymer by weight was obtained.

The NaAlg was then gelled by the application of $CaCl_2$ solutions. One batch of 1% NaAlg was gelled by spraying 15mL 10% $CaCl_2$ per 100g salt. A second was gelled using 65mL of 2% $CaCl_2$ per 100g salt. The 2% NaAlg was gelled by pouring the salt into a 5% $CaCl_2$ solution and allowing it to sit for 10 secs. The liquid was then drained and the salt dried by a heated air stream. The amount of $CaCl_2$ absorbed was then determined gravimetrically to be 1.35%.

The rate at which the solutions were sprayed was roughly equal to the rate of drying. This caused minimal wetting of the salt.

An estimation of the thickness of the CaAlg coatings was made. It assumed the salt to be perfect spheres and was done using the volume of a fixed number of particles and the density of CaAlg. The insolubility of CaAlg allowed the salt to be dissolved out leaving the intact CaAlg ghosts (empty film coatings) which could be collected and weighed. The solubility of HEC in water prevented the performance of this test on HEC coated salt.

The coated salts were also tested for caking to ensure that they would remain free-flowing, a necessary property if the salt is to be utilized. The

salt was placed in open bags in a humidity chamber at 22 deg. C and 100% R.H. for 48 hours. It was then removed and poured through a funnel with a 1 cm diameter neck. At this time it was also checked for any visible signs of hygroscopy.

The shortcomings of the conductance and road core tests necessitated that another means of evaluting the effect of the coatings be found. A test had been proposed by Slinkard (ref. p28) and was modified by us. It consisted of placing a fixed amount of deicing material on a contained block of ice of fixed dimensions. The amount of ice melted, under controlled temperature conditions, was determined at fixed time intervals. This gave an indication of the rate of dissolution of the salts since the amount of salt in solution would be indicated by the amount of ice melted.

The early work using this method was done using a preweighed cylindrical block of ice 8 cm in diameter and 1 cm thick giving about 50 g of ice (the 50 g block ice test). The temperature ofthe ice was equilibrated to-10 deg. C. Then 0.35 g salt (4-7 pieces) was spread over the ice (this is approximately 1.5 times the road application density in gm^{-2}) 4.5 times that normally used on the road. Samples were then removed after 10, 20, 30 and 40 minutes for the untreated salt, for the salt coated in 1% polymer, and in one case for salt with a 2% CaAlg coat. For the salt encased in 2% polymer samples were removed at 10, 25, 40 and 55 minutes. The brine was immediately poured off each sample and collected for volume measurement. The effectiveness of the different coatings was then evaluated using the relative volumes of brine obtained.

A test run consisted of four blocks of ice each treated with the same type of salt. There were five runs each of untreated salt, 1% HEC and 2% HEC, 6 of 1% CaAlg and 4 of 2% CaAlg.

It was observed that the salt characteristically melted the ice by boring a hole through it rather than by melting the ice in uniform layers. This phenomenon was studied by filling a set of test tubes with 10 cm of water and allowing the water to freeze. The tubes were then placed in a bath at 0 deg. C and allowed to come to thermal equilibrium. A preweighed piece of salt (either coated or untreated) was then placed in each and observed. The time taken for each piece to completely dissolve was measured as was the time taken for the salt to bore down a fixed distance.

4 RESULTS

4.1 Viscosity Enhancement

The results of the measurements of solution viscosities for GG, HEC, NaAlg, and PAA are illustrated in Figures 2-6. The viscosity of the 1% PVA solution (the only PVA solution measured) was six centipoise.

The first four of these show the effect of shear (which is proportional to spin rate in this case) on the viscosities of the 0.1%, 0.5% and 1% solutions. It should be noted that all these solutions exhibited shear thinning and that this shear thinning is more apparent at the higher concentrations.

The fifth of these figures shows the low shear viscosities of the various solutions in relation to one another. The logarithmic relationship between viscosity and concentration, as well as the relative positions of the lines at low concentrations should be noted.

The effect of viscosity on the rate of drainage through a road core sample is illustrated in Figure 7. It can be seen in this figure that the relationship appears to be one of direct proportionality.

4.2 Encapsulation

The coatings on salt formed by immersion in a polymer solution followed by the spreading out and oven drying of the salt were poor. The majority (90%) of the coatings, regardless of coating type, left exposed salt visible.

These flaws were also observed to accelerate the separation and deterioration of the coating when coated salt was immersed in water. These coatings were not strongly adhering to the salt and could easily be flaked off.

The results of measuring the effects of encapsulation on dissolution through the use of conductance are summarized in Table 2. The lower the slope of the line the more dissolution has been retarded. For these results to have meaning they must be compared with the value obtained for salt with no coating.

The coatings formed using the scaled down drum dryer could not be flaked off and adhered to the salt much better than those produced by manual coating. However, they still were, for the most part, incomplete (or on some particles non-existent), showing breakthrough of the salt. When immersed in water these coatings did not break up as quickly as those of the earlier encapsulation method.

The amount of the various drum dryer treated salts lost (as a % of the 10 g applied) while melting 25 g of crushed ice is summarized in Table 3. In order for the numbers to be meaningful it is necessary to compare them with those for untreated salt. The large standard deviations for the gel coated salts should be noted.

Judging qualitatively, the most successful coating method by far is the spray method. The coatings produced adhered to the salt and could not be flaked off. They left only 20% of the salt with breaks in the coating. When

the coated salt was placed in the water the salt could be dissolved out leaving an intact polymer ghost (an empty coating still retaining the shape of the particle it once coated; see Figures 11 and 12 for examples). The polymer ghosts from HEC encased salt dissolved completely within several hours while those of CaAlg salt lasted until they were broken down biologically. Even in the case where there was a break in the coating it was small and did not significantly speed up deterioration of the polymer shell.

The CaAlg salt which was gelled using a sprayed 10% $CaCl_2$ solution was hygroscopic. It and the other CaAlg gel formed using a sprayed on $CaCl_2$ solution had grainy consistencies. The CaAlg formed by briefly immersing the salt in a $CaCl_2$ solution absorbed 1.35% by weight $CaCl_2$. It was not hygroscopic and had a smooth consistency. It also dried ten times as fast as the sprayed CaAlg during the second drying.

The average thickness of the CaAlg coatings were determined to be $4x10^{-6}$m for the 1% coating and $1x10^{-5}$m for the 2% coating. The caking test showed no evidence of caking for either the HEC or CaAlg coated salt.

The results of the 50 g block ice tests are summarized in Tables 4 and 5. The large intercepts, similar slopes and low correlation coefficients in the results of linear regression analysis are significant. The large amount of overlap in the average values for the three salt samples is also significant as is the fact that the values reach a maximum and then decrease.

Figure 10 and Table 6 summarize the results for the 900 g block ice

tests. The slope of the best line (as determined through least squares regression through each sample's data serves as a measure of its dissolution rate. Note the high correlation coeficients.

High variability in the rate at which the salt moved vertically through the ice in the test tubes was observed. Much of this was attributable to faults in the ice since the salt tended to follow these. Rates of up to 2mm per minute were observed.

Table 7 gives a summary of the results of the tests measuring the time taken for the complete dissolution of salt particles in test tubes filled with ice. The high standard deviations are of importance as is the relative ordering of the dissolution rates when arranged largest to smallest.

5. DISCUSSION AND INTERPRETATIONS

5.1 Viscosity Enhancement

Non-Newtonian behaviour was observed in all of the polymer solutions (except for PVA since it was not tested due to its low viscosity). They were all observed to be shear thinning. This is advantageous for our purposes because it means the viscosities of the solutions on the road would actually be slightly higher than those measured because road drainage occurs under approximately zero shear conditions. Thus, the viscosities of the solutions plotted in Figure 6 are the lower limits of the practical viscosities. At lower concentrations, however, the practical viscosity would approach the measured viscosity due to the dependence of non-Newtonian behaviour on concentration.

It is apparent from Figure 6 that, at the low concentrations at which polymer would be found on the road (0.005% and 0.05%), NaAlg offers the greatest viscosity enhancement, yielding a brine 3 to 10 times more viscous. The other polymers have a negligible effect (increasing viscosity by only 10% at the lower end of the concentration range). It is apparent that of the polymers studied only NaAlg has any potential for use as a viscosity enhancer.

The low concentration thickening power of NaAlg is attributable to its ionic characteristics. Ionic polymer coils expand at lower concentrations due to the intramolecular charge repulsions.

Figure 7 shows that drainage through the road core sample is directly

proportional to viscosity as is expected theoretically. However, the rate of drainage appears so high that even the tenfold increase in viscosity offered by NaAlg would do little to increase the residence time of the brine. It would take less than 10 minutes to drain a 10 cm column of 0.05% NaAlg through a road core sample. There is a difference between actual roadways and the core samples since on a roadway the entire surface is restricted to draining through the shoulders. However, viscosity enhancement will be ineffective at slowing brine loss unless this difference is very great. Hence, we concluded that viscosity enhancement is an impractical method of reducing the amount of salt loss on open graded friction courses.

5.2 Encapsulation

From the tests done on the manually coated salt it was determined that encapsulation does hinder the dissolution of salt (and hence increases the duration of its activity on the road). This is evident from slopes given in Table 2. The smaller the slope in relation to that of untreated salt the greater dissolution has been retarded. The effect is observed to be greatest in the salts coated using HEC and the gel system. Because of this, all further encapsulation work was focused on these coatings.

It was also determined from this work that the manual coating method was not feasible on a large scale and that it yielded poor quality coatings. Thus, the drum dryer coating method was developed since this method is more easily adapted to an industrial scale.

It was felt that measuring the rate of dissolution of salt in a large amount of water was a good method to determine if dissolution was retarded but it was a poor method for simulating the environment where the salt is actually used. A more suitable test was that in which salt was placed on ice in a test rig and the amount of salt consumed in melting the ice was measured. The salt used in this case was coated using the drum dryer method. This improved the quality of the coatings from those obtained using the manual method. It can be seen in Table 3 that all coatings used reduced salt loss. HEC performs the best (losing only 60% as much as untreated salt) and is compared with the untreated salt in Figure 8. CaAlg performs second best (losing 70% as much as untreated salt). The large standard deviations noted for both gel systems is believed to be a result of the gel coatings being stripped off some of the salt particles during processing. It was felt that if the integrity of the coatings could be improved then these standard deviations and averages would both become smaller. The results of the mixed HEC - gel system samples showed these coatings to be less effective than HEC alone. As such these coatings were no longer pursued.

Since crushed ice was used in this experiment there was much variability in the surface area of contact between the salt and the ice. Also, the amount of salt used was over 350 times the normal application density. Thus, this test was judged a poor measure of what would occur on the road. Hence, it was decided that similar tests using solid blocks of ice without draining would be done at lower salting densities. To improve upon the integrity of the coatings being evaluated, this testing used the salt coated using the spray method. The coatings on this salt were felt to be the best obtainable due to

their good adhesion and low incidence of flaws.

The first of these block tests (50 g of ice) yielded results with so much overlap and variability that they were of little use. Linear regression analysis of this data showed poor correlation, similar slopes, and large intercepts so it was of little use. It can be observed in Table 4 that the values all reach a maxima and then decrease implying that the de-icing capacity of the salt has been surpassed. Thus, the time scale of the experiment should be shortened. The relatively large errors signified by the average values of the blank runs would be diminished by increasing either the salting density (and hence amount of ice melted) or the surface area salted.

The second block ice test used a larger block of ice, higher salting density, and shorter time scale. This yielded more useful results than those of the earlier test. Linear regression analysis yielded lines with high correlations and significantly different slopes. The rate of dissolution (and hence rate of loss) of the different salts should be proportional to the slopes of these lines. If this is true then we can use the relative slopes of these lines to calculate the relative rates of salt consumption. This is simplified by dividing the slopes of all the lines by the slope of the untreated salt. This gives a relative rate of consumption since the salt coated with 1% CaAlg, 2% CaAlg, 1% HEC and 2% HEC would respectively dissolve 0.88, 0.58, 0.71 and 0.48 times as fast as untreated salt. Thus, if 1 tonne of untreated salt were replaced by 1 tonne of 1% HEC treated salt, at the time that all the normal salt would have been consumed only 71% of the coated salt would be consumed since it dissolves only 0.71 times as fast.

It follows that these values may then be used to calculate whether or not coating the salt should be feasible since the total cost of the salt can be estimated as:

$$TC = RS(EC+SC)$$

where:

- TC is the total salting cost to be effective as long as 1 tonne untreated salt
- TS is the relative salt consumption for the treatment of interest (given above)
- EC is the environmental cost ($350) per tonne
- SC is the salt cost per tonne as estimated in Appendix A ($35 for untreated salt, $115 for 1% coatings and $155 for 2% coatings)

Using this equation per tonne are $385, $409.2, $292.9, $330.15 and $242.4 for untreated, 1% CaAlg, 2% CaAlg, 1% HEC and 2% HEC salt respectively.

The fact that these coatings did not exhibit caking is also significant since it means that the coated salt can be spread in the same manner as untreated salt. It also appears that hygroscopy can easily be avoided by not using concentrated (>5% $CaCl_2$) solutions for producing CaAlg.

The dissolution tests involving ice in test tubes yielded results which appear to be of little use. The rate of vertical movement of the salt through

the ice depends more on flaws in the ice than the coatings so this data was judged to be of little use. The standard deviations of the total dissolution times and particle weights indicate great variability within each set of data making the utility of this data questionable. There does, however, appear to be the same trend in the relative average rate of dissolution values as in the block ice tests. If we take the dissolution rate of untreated salt as 1, then 1% CaAlg, 2% CaAlg, and 1% HEC have the respective dissolution rates 0.90, 0.73 and 0.83. However, with the large variability within the samples only the relative ordering of these values can be considered important.

The results of the above testing lead one to conclude that improvement of the road life of salt on open graded friction courses using polymer encapsulation is feasible, and that HEC was the most suitable candidate studied for doing this.

6. REFERENCES

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W.E. Slinkard, "Sodium Formate - An Alternate Highway Deicer to Rock Salt", Internal Celanese Chemical Company Report, March 18, 1985.

TABLE 1: The size distribution of salt particles

PARTICLE SIZE (mm)	PERCENT OF TOTAL	CUMULATIVE PERCENT
16.0	0	.1
16.0 - 12.7	.3	.3
12.7 - 9.5	1.7	2.0
9.5 - 6.4	14.4	16.4
6.4 - 4.8	18.8	35.2
4.8 - 2.4	39.9	75.1
2.4 - 2.0	5.4	80.5
2.0 - 1.2	10.8	91.3
1.2	8.7	100

TABLE 2: The results of the conductance measurements

COATING	TEMP (°C)	SLOPE (mho/s)
None	2.8	3.36×10^{-6}
GG	3.5	2.25×10^{-6}
HEC	3.3	1.96×10^{-6}
Sodium Alginate	3.3	2.48×10^{-6}
PAA	3.0	2.93×10^{-6}
PVA	3.9	2.75×10^{-6}
Calcium Alginate	2.8	1.71×10^{-6}

TABLE 3: The salt lost in melting 25 g of ice (expressed as a percent of amount applied)

COATING	Salt Loss (%) AVERAGE	STANDARD DEVIATION
None	55.3	3.75
None[1]	59.5	3.62
HEC	33.5	3.80
Calcium Alginate	38.4	6.07
Guar Gum Gel	44.6	7.07
HEC + Calcium Alginate[1]	47.6	3.83
HEC + Guar Gum Gel	40.5	3.96

1. Indicates a different crushed ice source was used for these experiments

TABLE 4: The percentage of a 50 g block of ice treated as specified which was melted at the indicated time

TREATMENT	TIME (min)	Salt Loss (%) AVERAGE	STANDARD DEVIATION
None	80	1.8	2.5
	160	1.1	0.6
	240	1.3	0.4
	320	2.4	2.4
	400	2.8	1.7
Salt[1]	80	8.5	2.3
	160	13.8	2.8
	240	17.1	3.2
	320	20.6	2.6
	400	15.3	8.3
1% HEC Salt[1]	80	7.8	0.8
	160	14.5	2.6
	240	15.9	4.1
	320	19.2	2.7
	400	17.6	4.2
1% CaAlg Salt[1]	80	8.2	2.2
	160	14.5	2.5
	240	18.7	3.3
	320	17.6	3.6
	400	14.5	5.5

1. 0.35 g

TABLE 5: The results of a least squares linear regression performed on the data from the 50 g block ice test

TREATMENT	SLOPE (g/min)	INTERCEPT (g)	CORRELATION COEFFICIENT
None	0.00286	0.212	0.401
Salt[1]	0.02073	2.129	0.647
1% HEC Salt[2]	0.02207	1.836	0.844
1% CaAlg Salt[3]	0.01873	2.379	0.723

1. 0.35g
2. 0.35g salt coated in 1% by weight hydroxyethylcellulose
3. 0.35g salt coated in 1% by weight sodium alginate which was gelled by 1.3% $CaCl_2$.

TABLE 6: The best lines through the data obtained from placing 5 g of treated salt on a 900 g block of ice

COATING	SLOPE (mL/min)	INTERCEPT (mL)	CORRELATION COEFFICIENT
None	0.978	3.400	0.938
1% CaAlg	0.859	1.215	0.953
2% CaAlg	0.571	0.099	0.920
1% HEC	0.692	-0.840	0.998
2% HEC	0.470	0.536	0.987

TABLE 7: The average particle weights and times for complete dissolution for various coated salts when placed on ice

COATING	WEIGHT (g)	STANDARD DEVIATION	TIME (s)	STANDARD DEVIATION	RATE (wt/t) (g/s)
None	0.0979	0.0283	1880	1126	5.21×10^{5}
1% CaAlg	0.1013	0.0205	2152	282	4.71×10^{5}
2% CaAlg	0.1035	0.0212	2727	850	3.79×10^{-5}
1% HEC	0.1169	0.0270	2693	1249	4.34×10^{5}

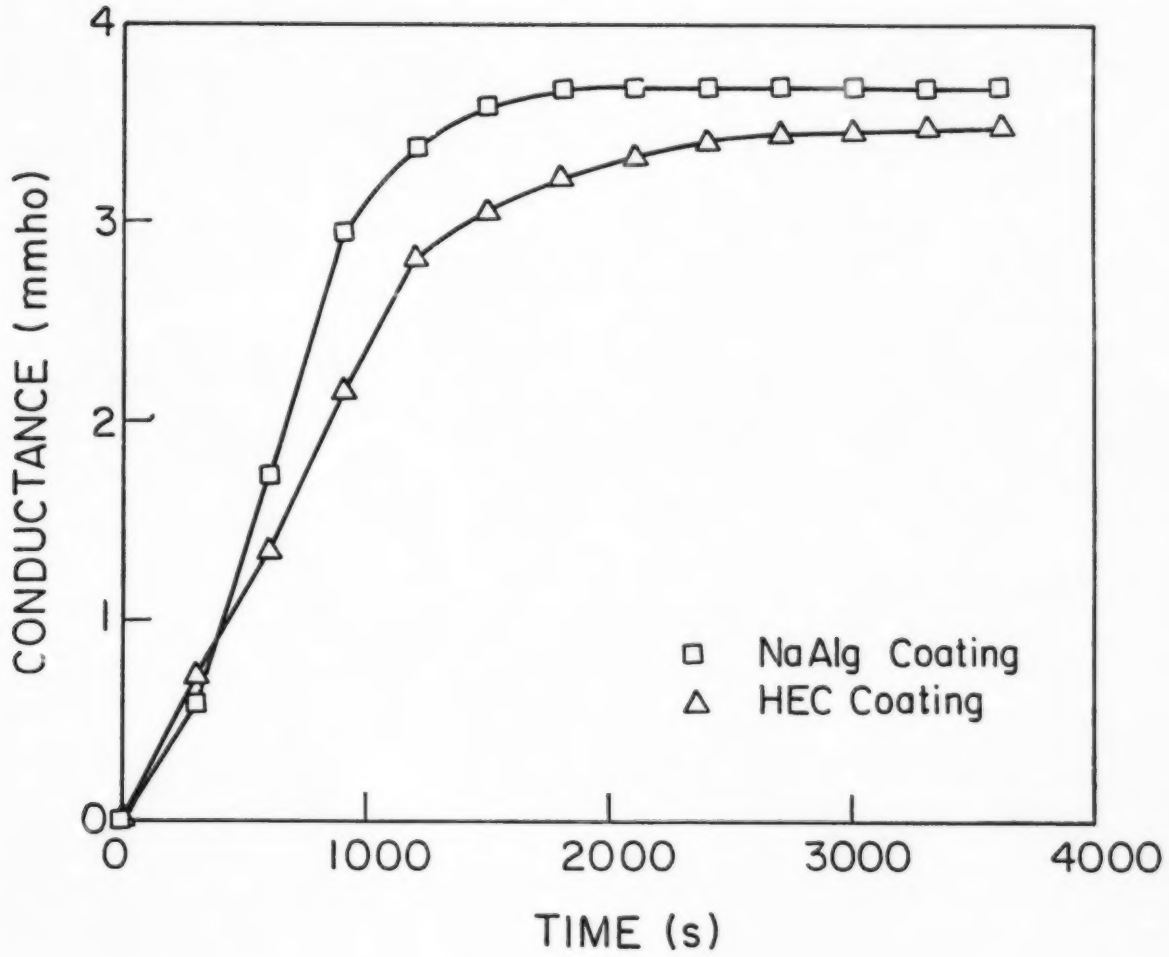

FIGURE 1: Typical Conductance vs Time Plots
for dissolution of salt in distilled water

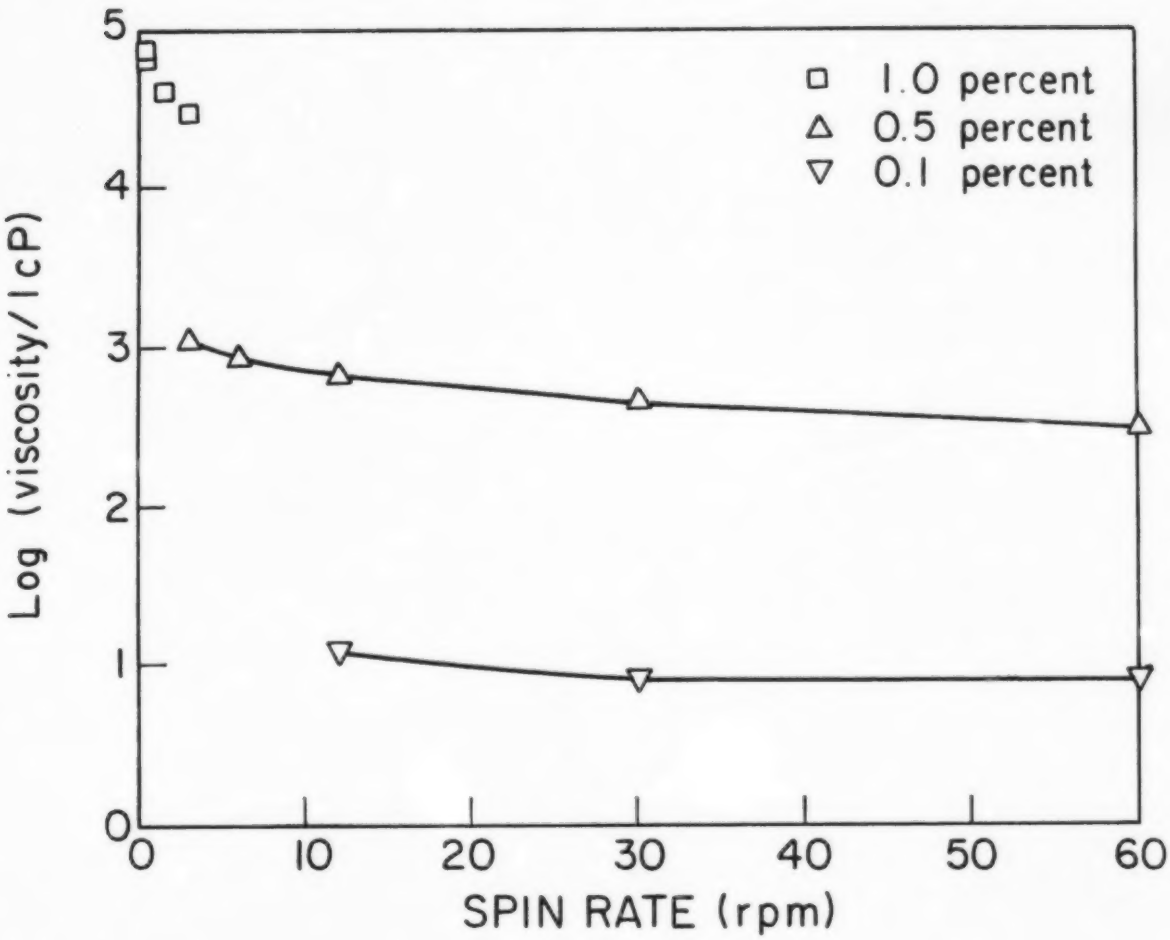

FIGURE 2: Viscosity vs Spin Rate for Guar Gum

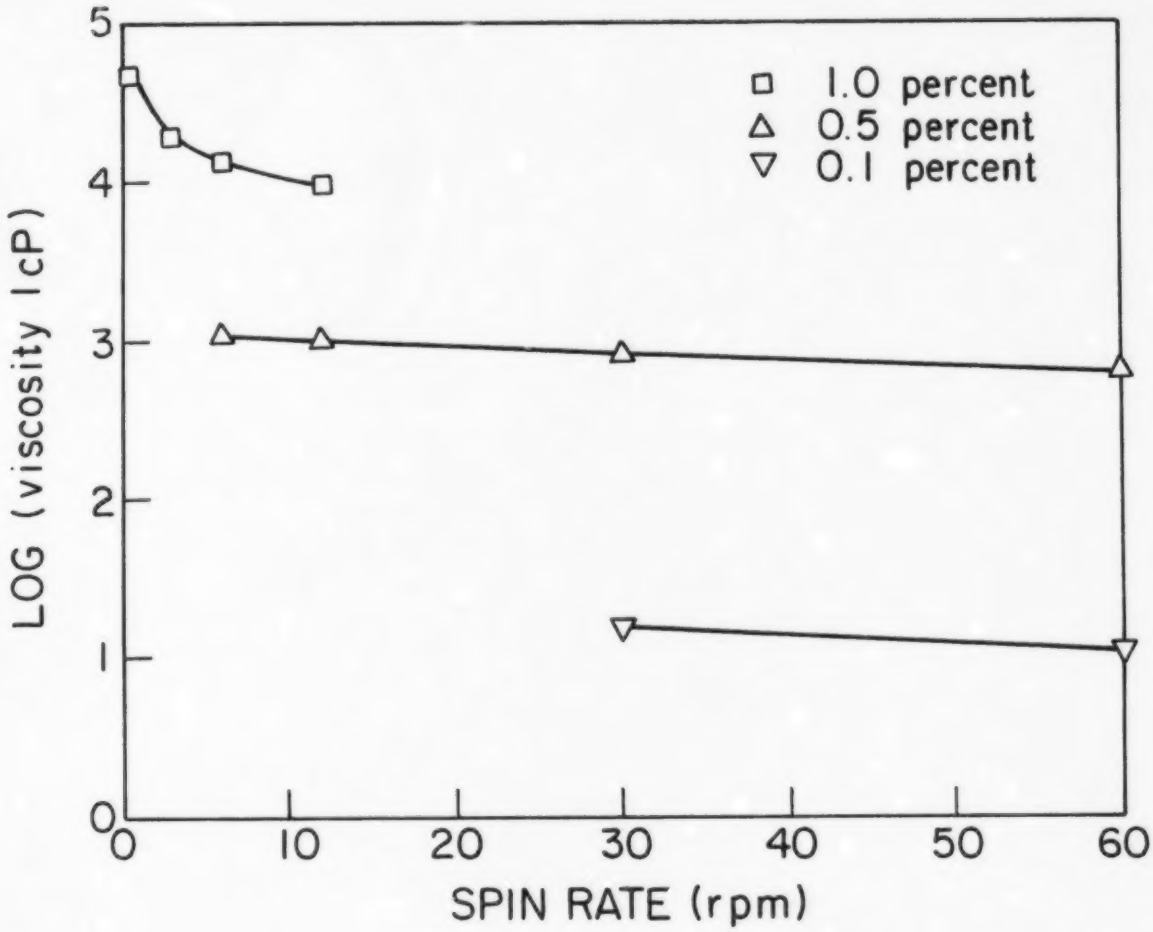

FIGURE 3: Viscosity vs Spin Rate for Hydroxyethylcellulose

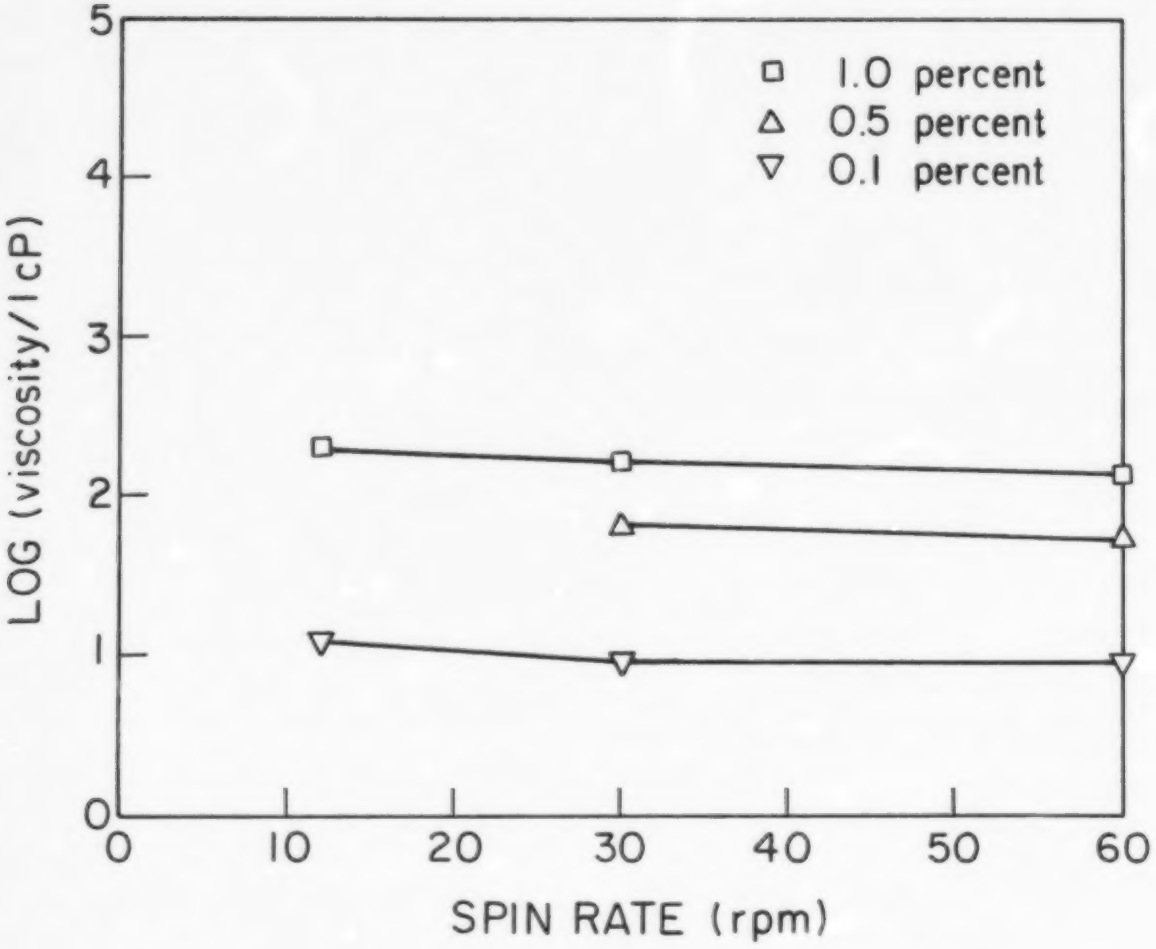

FIGURE 4: Viscosity vs Spin Rate for Poly(acrylamide)

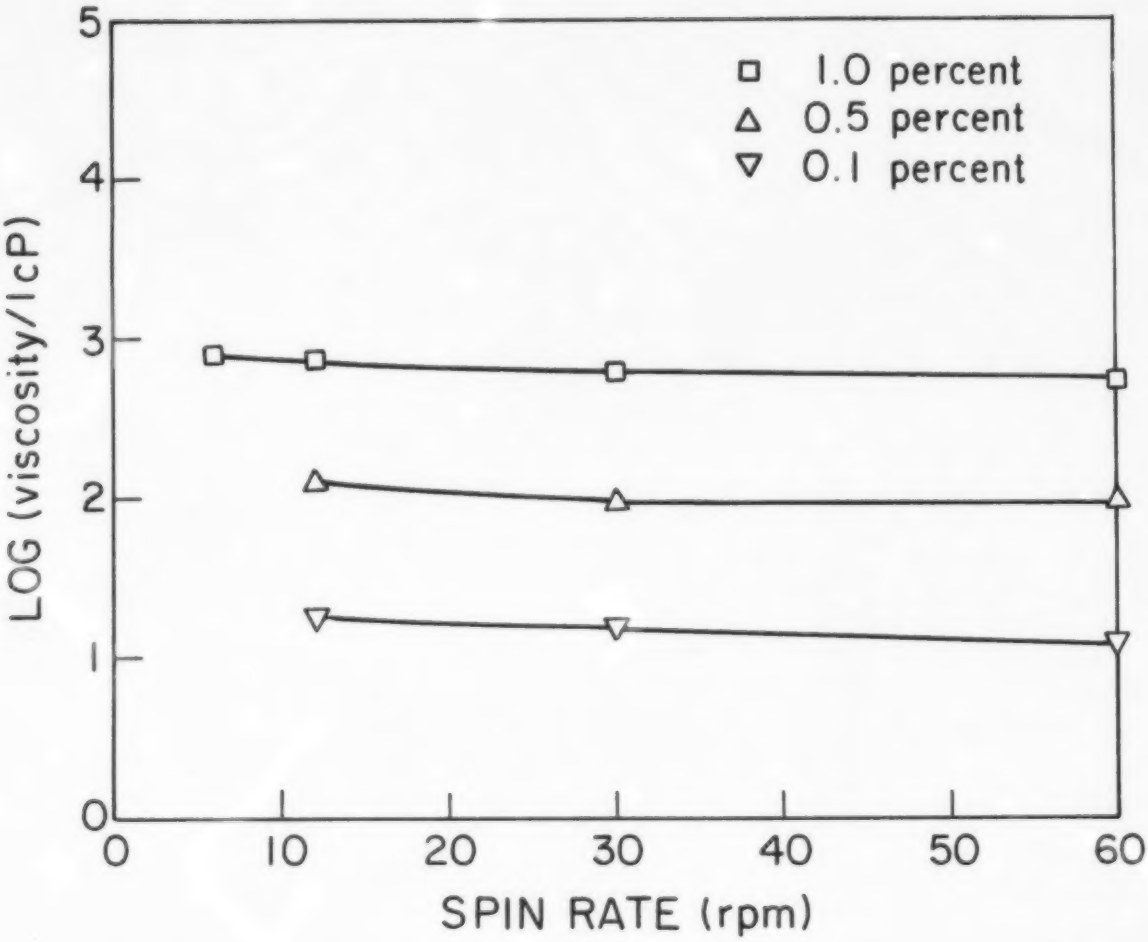

FIGURE 5: Viscosity vs Spin Rate for Sodium Alginate

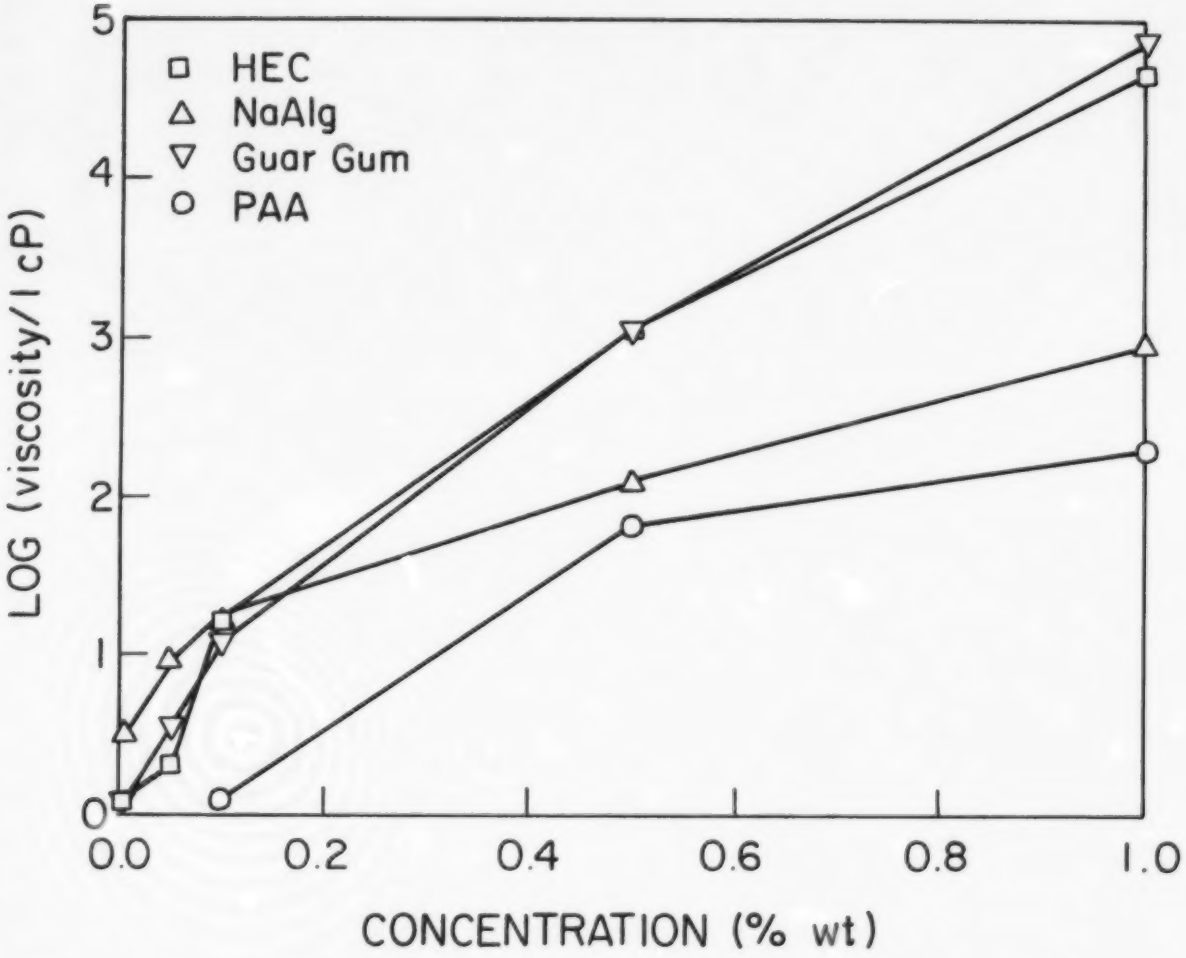

FIGURE 6: Low Shear Viscosity vs Concentration

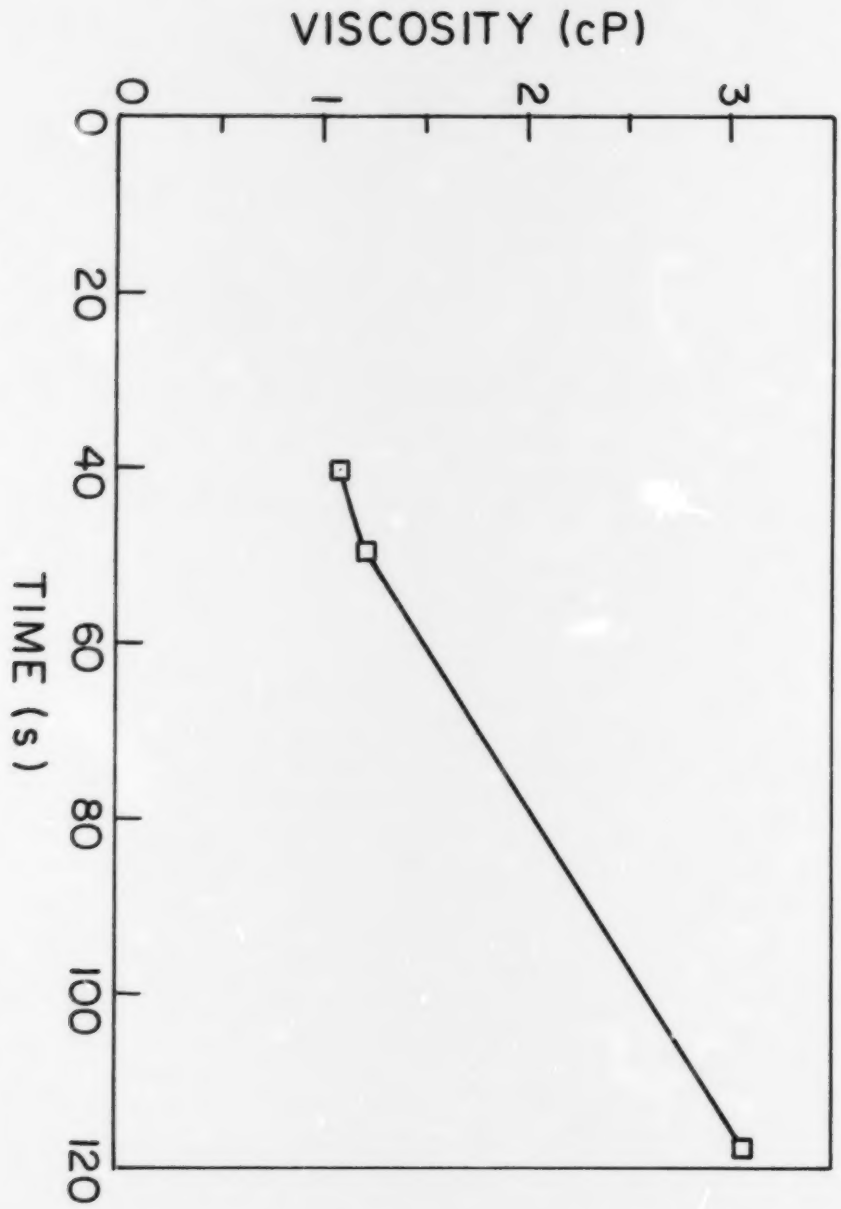

FIGURE 7: Viscosity vs Road Drainage Time for 150 mL solution through high porosity asphalt

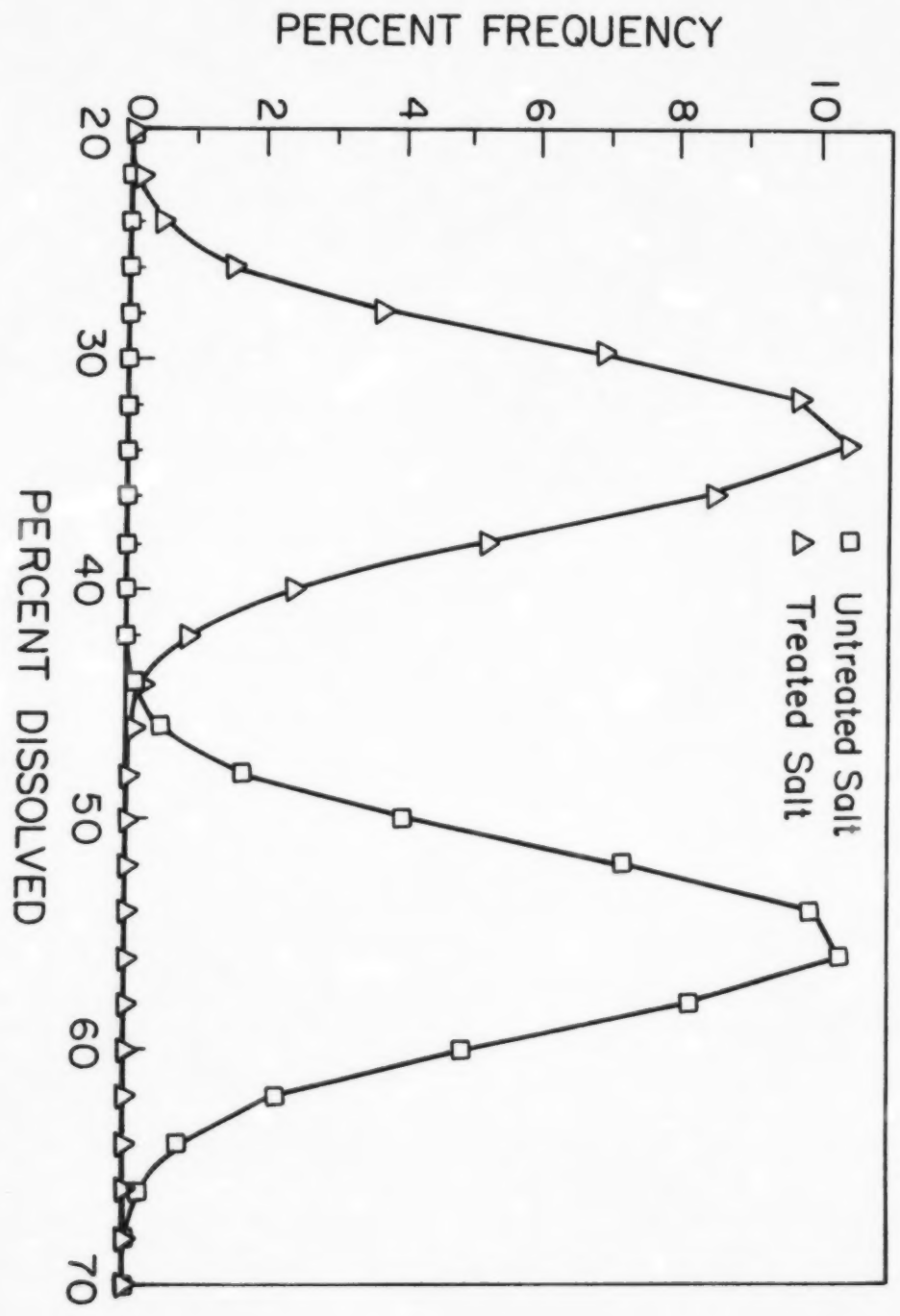

FIGURE 8: Distribution of Salt Loss
(from 10g starting material)

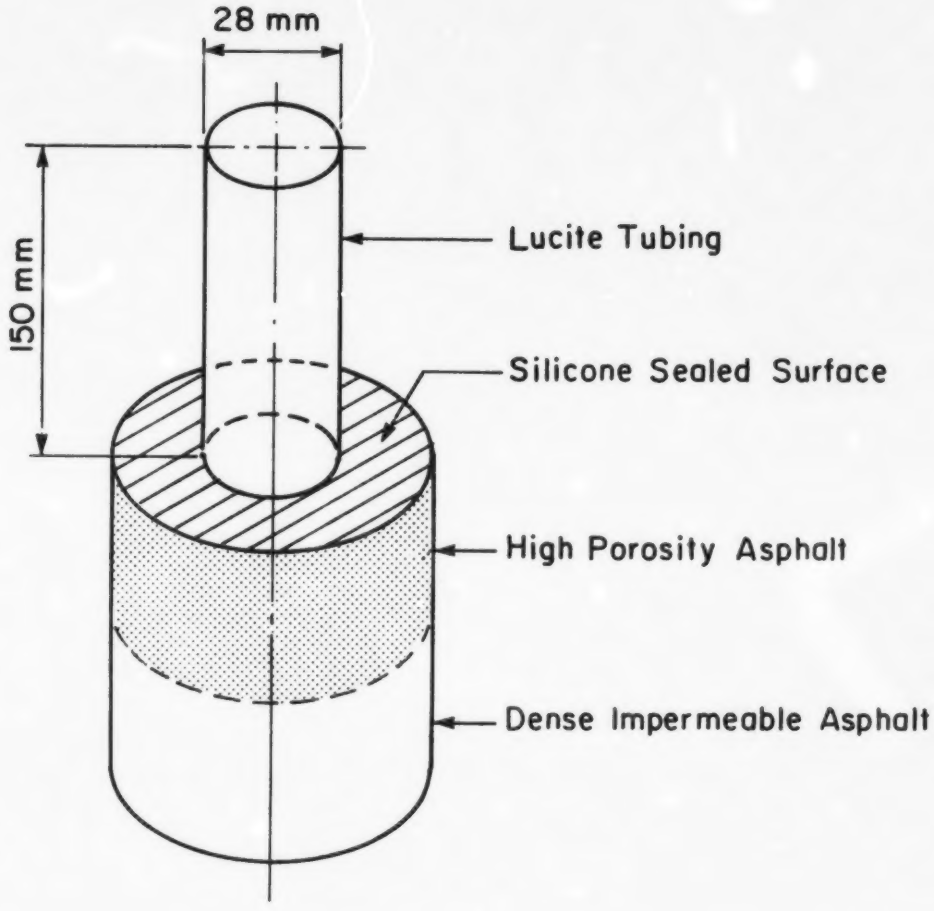

FIGURE 9: Diagram of a Modified Core Sample

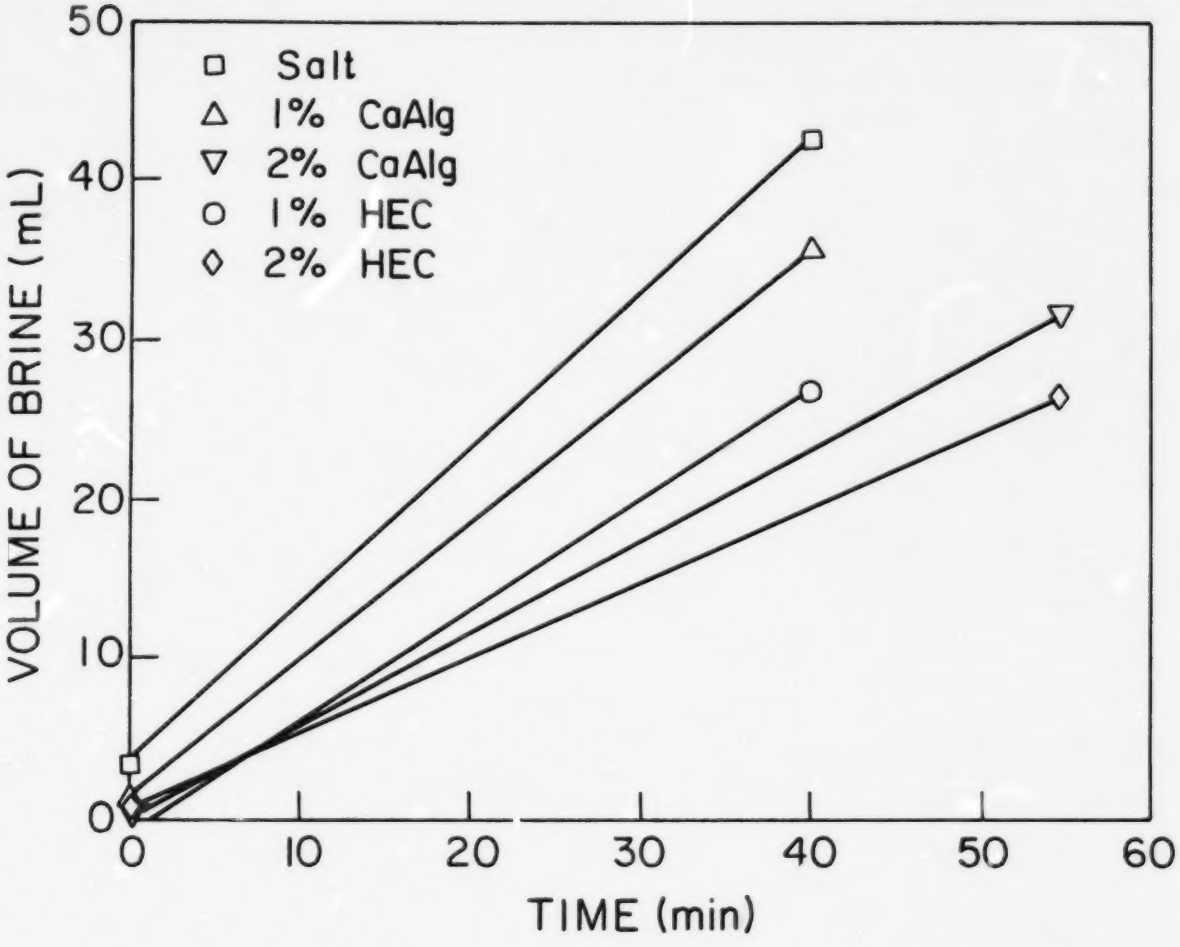

FIGURE 10: Ice Melted vs Time for 900g Block Ice Test

FIGURE 11: A photomicrograph of an intact Calcium Alginate ghost (10x magnification) prepared as a 1% by weight coating on salt using the spray coating method

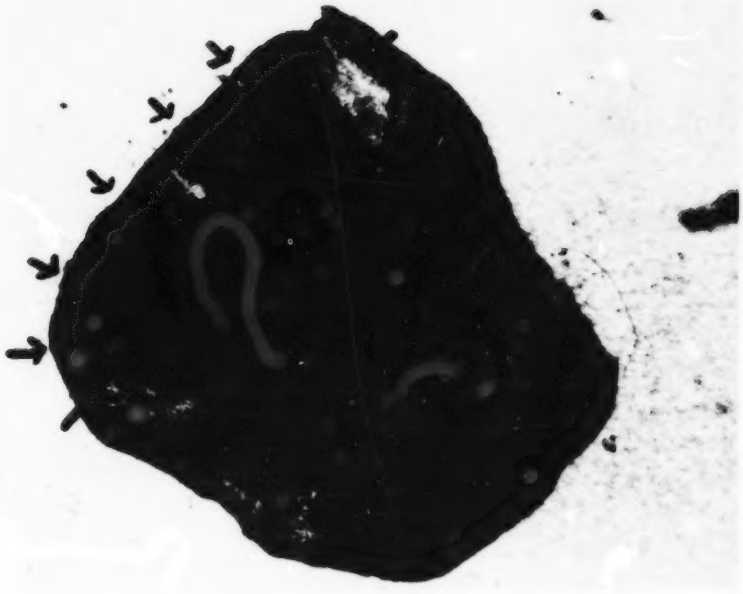

FIGURE 12: A photomicrograph of a flawed Calcium Alginate ghost (10x magnification) as a 1% by weight coating on salt using the spray coating method. The flaw is highlighted.

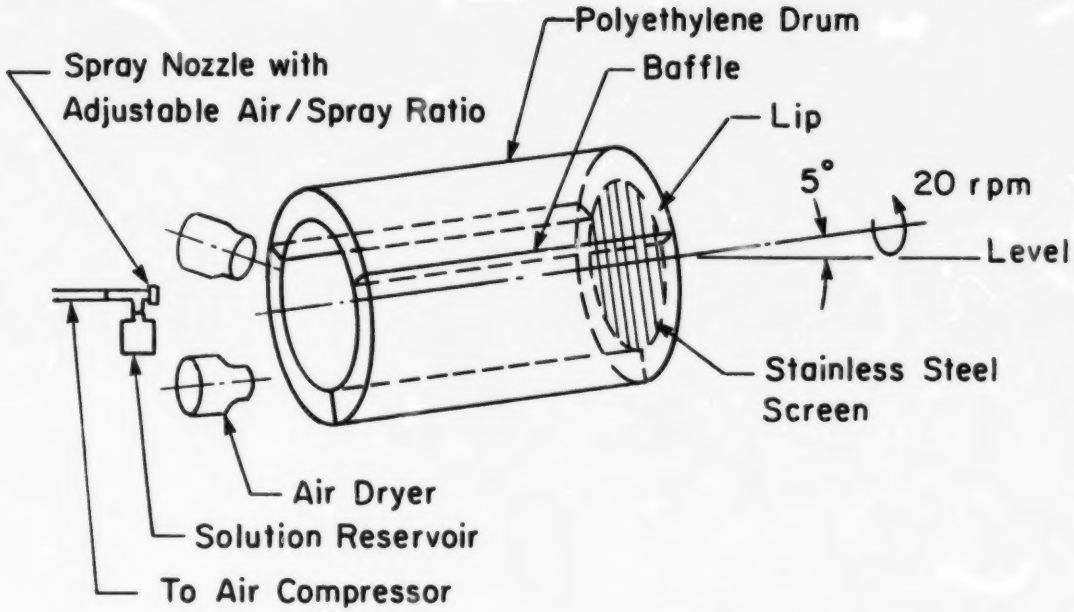

FIGURE 13: Diagram of the spray coating apparatus

APPENDIX A

ESTIMATION OF COST

Viscosity Enhancement

Water-soluble polymer costs approximately $6 a kilogram. Salt costs approximately $35 a tonne. Hence, if a salt-polymer blend, containing 1% polymer was made, then it would cost approximately 2.7 times as much as the normal salt. A 2% polymer blend would cost 4.4 times as much.

Salt is spread on the road at 160 kilograms per lane kilometer. This corresponds to 44 grams per square meter. If we assume it is to melt 1 cm of ice or 10 cm of snow then 10 litres of brine per square meter would be formed. This would contain 0.44% dissolved salt and 0.004% polymer.

Thus, the materials cost would roughly triple to get a polymer concentration on the road which may go as low as 0.005%.

Encapsulation

A maximum of 1000 litres of water would be needed to dissolve the polymer needed to encapsulate 1 tonne of salt in polymer at 1 by weight. Water requires 540 kilcalories per litre to be converted into steam. The combustion of propane yields 7,000 kilcalories per litre. Thus, each litre of propane can vapourize 13 litres of water. Hence, approximately 75 litres of

propane would be required to dry 1 tonne of salt. Propane costs about 25 centre a litre. This means it would cost about $20 to dry a tonne of salt.

Using this information and the costing done in the previous section, the cost of 1% polymer encapsulated salt can be estimated to be 3.3 times the cost of untreated salt, and a 2% polymer encapsulated salt can be estimated to cost 5.5 times as much.

APPENDIX B

THE UNUSUAL DRAINAGE CHARACTERISTICS OF OPEN GRADED FRICTION COURSES

The effect of the head on the flow rate though the road core samples was examined. To do this a ruler was attached to the reservoir of two road core samples. The zero mark on scale was approximately 5 mm above the road surface. Thus, all the values for the head, given in Figures A and B are given relative to this zero. Figures A and B clearly show that the flow rate of water through the road cores is not only dependent on the head, but also on the amount of liquid drained directly preceeding the measured flow (this is indicated by the amount of time liquid was allowed to drain prior to flow rate measurement). Antecedent flow seems to decrease the flow rate through the core samples. This cannot be entirely attributable to a wetting effect since Figure B shows the results for a core sample immersed in water for 10 days previous to its use. If flow has occurred uninterrupted prior to the measurement of the flow rate then several measurements will be similar to those plotted in Figurea A and B. If the flow is interrupted then the flow rate will rebound.

This unusual property requires further investigation if drainage through the road surface is to be fully understood.

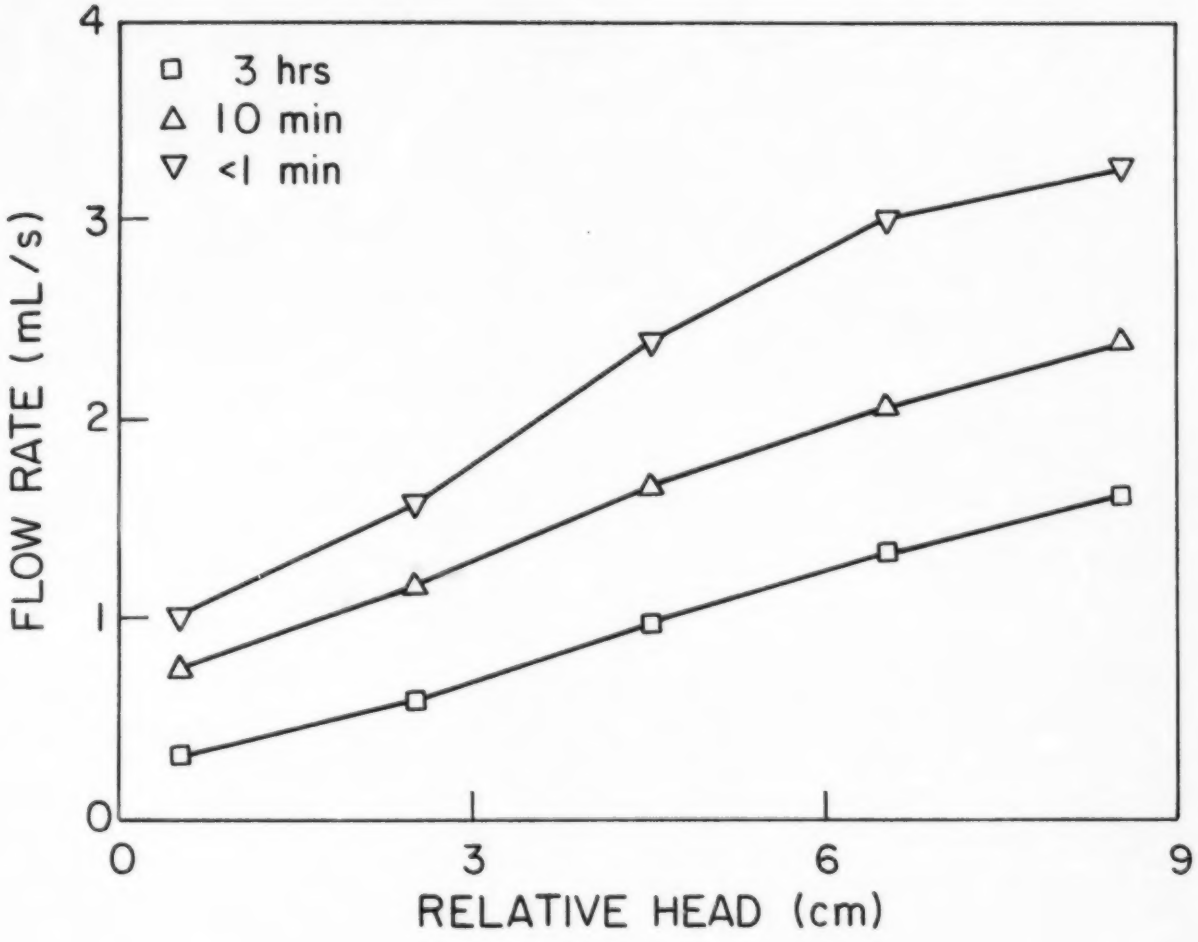

FIGURE A: Flow Rate vs Relative Head starting dry

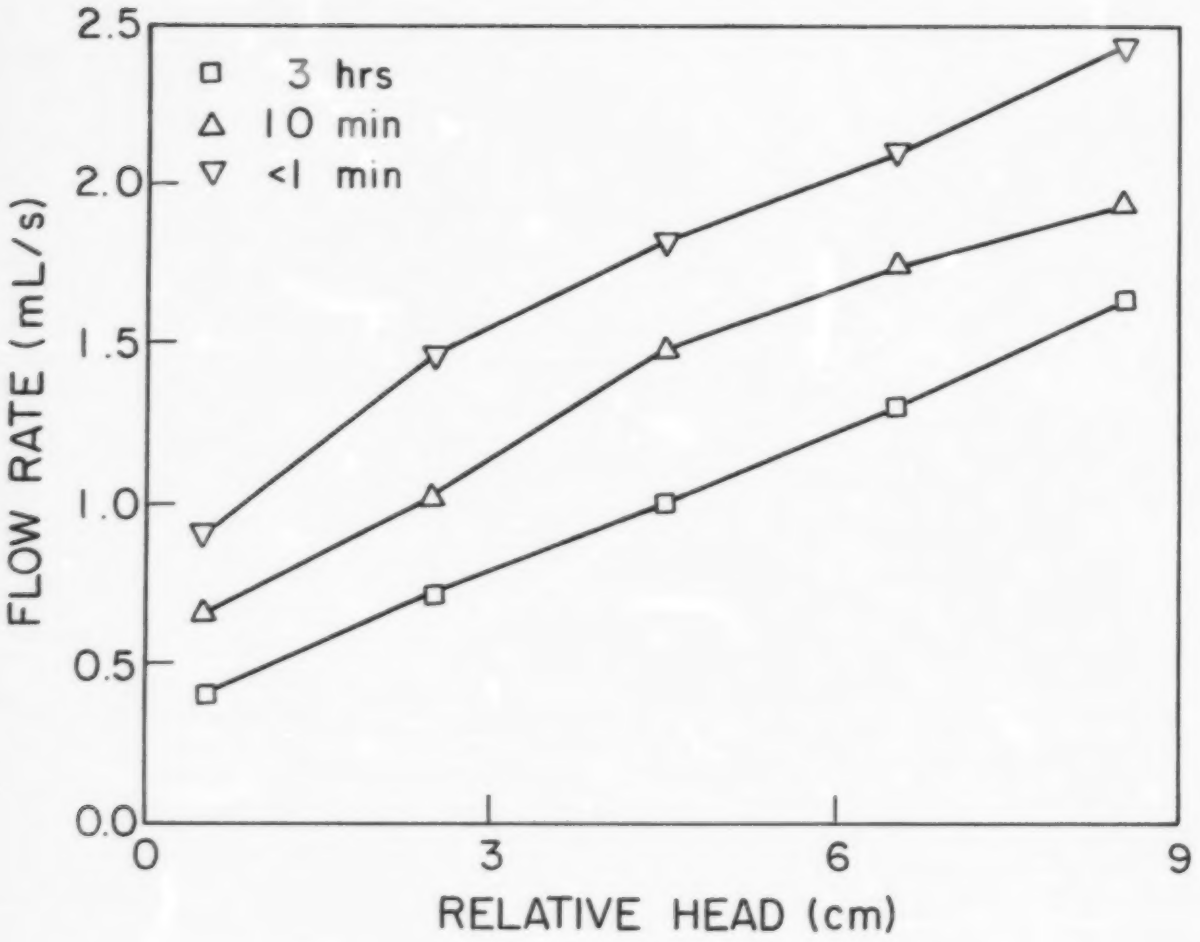

FIGURE B: Flow Rate vs Relative Head after 10 days immersion